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Biogas plants as key units of biorefinery concepts: Options and their assessment

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ABSTRACT

In order to minimize the environmental impacts of growing population, progressive exploitation of fossil resources and negative consequences of climate change the politically intended goal is to successively transform our primarily oil-based into a bio-based economy. Hence, one goal is to significantly reduce the utilization of fossil resources by increasing the use of renewable energy and resources (i.e. biomass) and the efficiency of their conversion processes. Including existing technologies into the development of future concepts could accelerate the transition to a bio-economy. As one solution integrated biorefinery concepts based on agricultural biogas plants are discussed, which convert biomass with minimal energy consumption to a multitude of products without generating waste. However, they still have huge potential in terms of increased biomass utilization. In that context, catch crops offer interesting opportunities as a substrate for those biorefineries, since they support soil regeneration while generating additional products for the bio-economy without increasing land use. In this study a selection of significant indicators was chosen in order to determine the environmental effectivity and economic efficiency of these biorefinery concepts by a systematic assessment of possible process schemes. Thus within this study the usability of the chosen indicators and the potential of catch crops in advanced biorefineries is assessed.

1. Introduction

Climate change, steady population growth as well as still considerably growing use of non-renewable resources are some of the major challenges of this century. One way to counteract these challenges is to transform our primarily fossil resource-based economy step by step into a bio-based economy. This might go hand in hand with slowing down global warming because the use of bio-based materials does contribute only to a very limited extend to the global greenhouse effect. Thus the European Union (EU) estimates that the utilization of biomass in general (material and energy uses) could save globally CO_2 emissions in the order of 2.5 bn. t/a CO_2-equivalents until 2030 (European Commission, 2015). For example, the coverage of the German energy demand (both heat and electricity) only by biogas is estimated to possibly increase from 2% today (German Association of Biogas Specialists 2017) up to 13% (Brosowski et al., 2016) within the next decades. However, the rise in conventional biofuels (bio-ethanol from starch or sugar, -diesel from oilseeds and -gas from starch and oil) was slowed down in 2010 by the realisation that their competition with food production is to be avoided (The U.S. Energy Information Administration, 2016). Therefore, research efforts have been focussed on advanced biofuels either by their production from alternative feedstocks like residual streams or alternative production processes (International Energy Agency, 2011).

Apart from reducing greenhouse gas (GHG) emissions, another objective of such a bio-economy based on a significantly increased use of biomass for energy and materials is to replace conventional crude oil based processes or products respectively by ones based on renewable biogenic resources characterized by a significantly lower effect on global climate (i.e. decarbonisation of our overall economy). In parallel a sufficient food production (i.e. plant material as well as animal-based food components) need to be guaranteed (Oborne, 2010; The White House, 2012). In this context, modern, integrated biorefineries represent a key concept to achieve these ambitious goals (Federal Government of Germany 2012).

So far, the assessment of such biorefinery concepts is realized primarily product-orientated by focussing e.g. on theoretical biomass conversion efficiencies (e.g., Nova Institute (Iffland et al., 2015)). Thus, here an application-orientated assessment for the transformation of conventional biomass conversion processes into integrated biorefineries

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is presented applicable to existing biomass conversion respectively biorefinery plants. To demonstrate the applicability of this approach the proposed method is applied to decentralized biogas plants as an example for the assessment of biorefineries to be implemented in the years to come.

2. Small scale biorefineries

The aim of a biorefinery is to utilize the available sustainable biomass as complete and as efficient as possible to provide a broad range of high value marketable products with minimal energy consumption and without creating waste streams. Below a short summary regarding the classification of such biorefineries is given, taking existing and new biorefinery concepts into account. Based on this some assessment indicators for such concepts are defined.

2.1. Classification

Biorefineries can be classified by its feedstock (e.g., energy crops, agricultural and forestry residues, food waste, algae), products (intermediates / final products to be sold to the markets for food, feed, energy, chemicals and/or pharmaceuticals) and/or processes (e.g., thermo-chemical conversion, biochemical conversion, physico-chemical conversion; for further information see (Zinoviev et al., 2010; International Energy Agency, 2011)).

Additionally the following key features are generally assigned to biorefineries:

- Multifunctional concepts with high levels of process integration and reduced demand for energy and auxiliaries.
- Any bio-based raw materials can be used; for innovative concepts non-food materials are to be preferred (e.g. residues, waste, by-products, energy crops).
- Raw materials are converted into a market driven wide range of products. In principal products intended to be used in the food / fodder market as well as within the markets for raw materials are preferred over a purely energetic use.
- Biogenic raw materials should be used completely; no or only very little waste streams are produced.
- The use of toxic and/or hazardous reagents and solvents is avoided as much as possible.
- The concept should typically be as flexible as possible towards changing markets for feedstock (i.e. input side) as well as for products (i.e. output side).
- The environmental burden (e.g. emissions in air, water, spoil, waste, noise) should be as low as possible.
- The social acceptance should be as good as possible.

Biomass is a priori a limited and decentralized available resource used traditionally within the markets for food, raw materials and energy on a global scale. To serve all these markets based on limited fertile agricultural land in a cost efficient and social acceptable way, the land needed for the various biorefinery concepts has to be taken into account as well. For instance, the carbon footprint of proteins from beef and seafood is by a factor of 14 to 150 and the land use by a factor 52 to 210 higher compared to the carbon footprint of their plant-based substitutes (Nijdam et al., 2012). Among other reasons, that is why the utilization of organic waste streams from various sources throughout the overall provision chain (e.g. agricultural residues like straw, processing residues like rice husks, distribution losses like waste from fruit markets, or municipal organic waste) as well as catch crops is typically recommended not only for soil protection but also for a land-use neutral biomass provision (Federal Statistical Office, 2003; Schuster et al., 2015; Federal Statistical Office, 2016).

Consequently, new innovative biorefinery concepts that are technologically feasible to be integrated into current agriculture and/or biomass processing industry, and thereby increase energy and biomass utilization efficiencies, are promoted by various governments. This is especially true for small scale decentralized applications due to the fact that biomass availability is strongly correlated with the available agricultural land and the transport of residues is typically cost intensive due to the often very low area-specific yield and the low value of such material streams.

One versatile type of such a biorefinery concept already widely used in Germany is the anaerobic fermentation of biomass in biogas plants located in the country side and characterized by moderate conversion capacities. This conversion option can act as a sink to degrade basically any kind of organic waste material (exception: untreated lignocellulosic biomass) into a widely useable energy-rich biogas (Hendriks and Zeeman, 2009; Lübken et al., 2010). Hence, due to typically very low requirements regarding the input substrates and a broad product spectrum possibly to be provided based on the produced biogas, such biogas plants can act as a core component of advanced innovative biorefinery approaches realized on the small scale decentralized within the country side (i.e. at locations where the biomass waste streams are easily available at low costs).

2.2. Assessment indicators

For a first rough assessment of such innovative small scale biorefinery concepts a selection of significant assessment indicators has been chosen in order to exclude inefficient and less promising concepts right at the beginning and thus to facilitate as well as to accelerate an effective process design. Therefore, technologies and production steps are compared by their technological, economic and environmental performance. Consequently, below these characteristic indicators are presented in detail, selection from (Dieckmann et al., 2018).

2.2.1. Technology readiness level (TRL)

A novel technology's stage of development is commonly described by the technology readiness level (*TRL*) as defined by DIN ISO 16,290 (see also (Jungmeier et al., 2014)). Within this approach the development of a technology or process is subdivided into 9 steps from early development stages (laboratory scale; *TRL* 1 to 3) over pilot stage (*TRL* 4 to 5), demonstration scale (*TRL* 6 to 7) to industrial scale (*TRL* 8 to 9). In a concept consisting of several conversion steps / phases / components, it is always the lowest *TRL* that determines the *TRL* of the overall biorefinery.

2.2.2. Variation of substrate value (VSV)

To include an economic component into the assessment of such innovative biorefinery concepts the so called substrate value (*VSV*) is defined. This characteristic figure describes the increase in value of an input substrate by its conversion to various products within such a biorefinery. For simplification any capital or operating expenditures are not taken into account. Thus, for each process step the ratio of revenues of products $R_{P,i}$ provided from the used feedstock price R_F including the individual mass m_i of product or feedstock is calculated (Eq. (1)). These values are then summed up for the overall conversion process / the overall biorefinery (Eq. (2)).

$$VSV_i = \frac{m_{P,i} R_{P,i}}{m_f E_F} \tag{1}$$

$$VSV_{total} = \sum_{i=1} VSV_i \tag{2}$$

2.2.3. Biomass utilization efficiency (BUE)

To support waste minimization and sustainability in the development of new production processes for fine chemicals the E(nvironmental)-factor has been developed. This key figure describes the ratio of produced waste streams per kg of product. Consequently, a high E-value corresponds to larg waste production and thus a stronger impact on the

natural environment (Sheldon, 2007). The atom utilization / efficiency of a process describes the molar ratio of atoms in the product related to the substrate. This key figure can serve as an indicator of low-waste processes when the ratio is close to 100% (Sheldon, 2007). Both key figures have been further developed towards the biomass utilization efficiency (*BUE*). This characteristic value is the mass-specific equivalent to the atomic efficiency. It further differentiates between the energetic (BUE_E) and the material product utilization (BUE_M) (Iffland et al., 2015).

- The BUE_M is calculated as the sum of the mass of various products $m_{P,i}$ divided by the mass of the feedstock m_F (Eq. (3)).

$$BUE_M = \frac{\sum_{i=1}^{n} m_{P,i}}{m_F} \tag{3}$$

- The BUE_E is calculated as the mass m_E in the provided energy carrier (e.g. biogas) divided by the mass of feedstock m_F (Eq. (4)).

$$BUE_E = \frac{m_E}{m_F} \tag{4}$$

2.2.4. Demand for auxiliaries (DfA)

The demand for auxiliaries (heat, electricity and chemicals, e.g. catalysts or solvents) is defined as the amount in kWh (for heat / electric energy) or kg (for chemicals) per metric ton of overall feed and each processing step. These data are based on literature, from experimental studies and / or information from manufacturers.

Based on these characteristic values, the assessment can be done based on individual processing steps. They are evaluated and the individual results are summed up to obtain the evaluation for the overall process. This is possible because the overall basis of the calculation is always the feedstock including the mass balance of the process.

3. Biorefinery concepts based on existing biogas plants

By developing new biorefinery concepts, existing structures and available biomass conversion facilities should also be taken into account as much as possible to pave the road towards a fast transition. As part of such biorefinery concepts, the biomass could initially be used for the production of valuable materials and the remaining organic residues could be fed into an anaerobic fermentation process to be converted into biogas (i.e. the biogas plant can act as a general sink converting the organic by-products / residues / wastes into a valuable energy carrier) (Zinoviev et al., 2010). Thus below the conventional agricultural biogas plant is explained. Afterwards, possible alternative substrates as well as products to be provided based by such an agricultural biogas plant are combined in innovative concepts and analysed.

3.1. "Classical" agricultural biogas plant (reference case)

The majority of the roughly 8500 biogas plants currently under operation in Germany convert the organic feedstock (78% of all biogas substrates are energy crops used of which 57% are corn silage, mostly in combination with animal manure) into biogas as an energy carrier for the subsequent generation of electricity and district heat within combined heat and power plants (CHP) (Daniel-Gromke et al., 2018) (Fig. 1); i.e. heat and electricity are typically the only valuable products to be sold on the market from such conversion plants. To allow for a trouble-free operation, the biogas provided by the anaerobic treatment within the fully steered reactor needs to be cleaned (e.g. hydrogen sulphur removal by microbial oxidation to elementary sulphur).

The digested slurry (digestate) contains still all components originally contained within the input feedstock and not degraded within the anaerobic treatment process. Depending on the technical realization of the biogas process this might be true for some specific types of

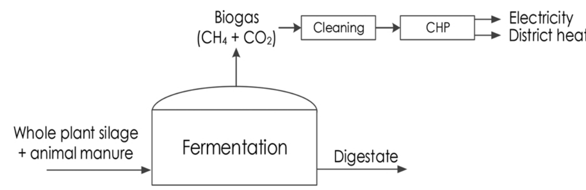

Fig. 1. Schematic flow chart of a conventional biogas plant.

biopolymers (e.g. lignin) as well as the inorganic constituents (N, K, P and others) of the biomass. Additionally, microorganism / biocatalysts realizing the anaerobic degradation process are still contained within the digestate. This digestate is typically used directly (i.e. without any further treatment) as a liquid fertilizer on agricultural land.

3.2. Alternative substrates and biomass constituents

In "classical" agricultural biogas plants the input material is so far digested directly within the biogas plants. But alternatively the input material can be used initially as a feedstock for the production / separation / provision of high value products contained naturally within the biomass (e.g. proteins, lipids, enzymes, colorants etc.). Under these conditions only the organic residues remaining after such a pre-processing step for the removal of such specific biomass ingredients would then be used as a feedstock for the subsequent biogas production. But also the digestate, which is often directly used as a soil conditioner on agricultural land, can be further processed to recover valuable products (e.g. nitrogen fertilizer, lignin, compost); such a post-processing of the digestate might enhance the storability of the provided products and/or to improve their targeted application, prevent eutrophication and generate additional increase in value of the substrate compared to the un-processed digestate. Against this background below first the various substrate groups and then important biomass constituents are discussed in detail.

3.2.1. Substrate groups

In addition to "conventional" biogas substrates (e.g. animal manure, corn silage, i.e. the most important energy crop used as a biogas substrate in Germany), alternative crops as well as other organic residues, by-products or wastes can be used for biogas production in theory. Important substrate groups are briefly enumerated below.

- Residues, by-products and wastes
  - ○ Agricultural production residues (e.g. different kinds of straw, animal manure).
  - ○ Agro-waste streams from food processing (e.g. potato peels, rice husks).
  - ○ Waste materials from food distribution (e.g. overlain food from supermarkets).
  - ○ Solid organic wastes from municipalities (e.g. restaurant waste).
- Speciality crops
  - Catch crops, like leguminens (e.g., clover), grasses (e.g., pasture grass) or crucifers (e.g., mustard) are commonly used for soil protection to prevent leaching losses or even to increase the nitrogen content in the soil (e.g. clover binds nitrogen from the air (ecoprog 2016)).
  - Crops with special ingredients (like active pharmaceutical ingredients, colorants, fragrants or spices) grown so far for provision of the desired impurity (although these desired components usually contained only with tiny fractions within the overall plant hey usually are (very) high in value; and lots of organic waste is provided to provide the desired ingredient).

3.2.2. Biomass constituents

Aiming to maximize the monetary value of the used substrate by

means of integrated biorefinery conversion processes, the composition and structure of the biomass need to be understood clearly since this determines the pathway that is taken for the valorization of the following biomass constituents and their respective application. Thus below important groups of biopolymers contained in organic material are presented and briefly described.

- Saccharides (also commonly named holocelluloses) occur in plants either as structural polysaccharides, like cellulose and hemicellulose, or storage carbohydrates, like starch or mono-/dimeric sugars. Mono- and di-saccharide applications in industry include food, feed and pharma whereas polysaccharide applications are also found in papers, textiles, cosmetics and pharmaceuticals. Furthermore they can act as platform chemicals to produce a variety of so far oil-based intermediates (Taylor 2015).
- Proteins consist of 20 essential amino acids that are linked by peptide bounds in a biomass-specific sequence. Like carbohydrates, they can exist as structural proteins in individual cells as part of the DNA and the cell membrane or the molecule chains form three-dimensional structures inducing bioactivity (i.e. enzymes). Proteins recovered from biomass are so far mainly applied in food and feed industry.
- Lipids are a part of the cell membranes in living organism and also serve as an energy storage. They can be divided into neutral, storage lipids consisting of fatty acids bound to glyceride and into polar lipids (e.g. phospholipids), which are surface active components and provide substantial parts of cell membranes. Together with wax and resins this group of molecules is often summarised as extractives (in ethanol, acetone or hexane). However, it is desired to use a description that focuses on the chemical structure and its application rather than the solubility. Further, this fraction's mass share in the used substrates of this work is negligible. The major share of lipids from plants is used within the food and feed industry. Other markets include the (chemical) industry (mainly the pharmaceutical and cosmetic / pharmaceutical sector) as well as the energy sector (e.g. biodiesel) (Mielke, 2017).
- Lignin is, besides cellulose and hemicellulose, one of the main components of lignocellulosic biomass and therefore the part of plant cell walls providing stiffness and resistance against microbial degradation (also anaerobic fermentation) (Saake and Lehnen, 2000; Rubin, 2008). It consists of methoxy-substituted phenyl-propanol subunits. Consequently, lignin is the most abundant renewable resource of aromatic compounds. Properties can vary strongly depending on the employed extraction / production methods. Hence, its applications vary strongly (e.g. binder (in pellets, polymers), active filler (e.g. in adhesives), colorant, lubricant, dispersant (if water soluble like lignosulfonates)). However, in industry these applications are rarely implemented, thus lignin is often burned e.g. in paper mill's lime kilns for energy recovery (Biermann, 1996; FAO 2015).
- Inorganics are essential elements (minerals or nutrients) that are needed in any plant for the regulation if its metabolism (Bresinsky et al., 2008) as well as inert material such as SiO_2. Different to macronutrients like C, H, O, which are mainly absorbed from air / water, the micronutrients / minerals (mainly N, P, K but also Mg (and trace elements like Mn, B, Zn)) are removed from the soil. However, on highly cultivated agricultural land the supply of minerals is often insufficient due to removal by harvesting or leaching. In order to counteract this effect, mineral fertilizer are added to the fields. Thus a competitive fertilizer with clearly defined ingredients produced e.g. from the digestate would find easily its way to the existing fertilizer markets.
- Active natural components, also known as secondary plant components, comprise of a wide range of molecules that can be used for colouring (e.g. benzoquinones in Safflower), odouring (e.g. terpenes from Caraway), flavouring (e.g. aromatic compounds from sweet clover) or even natural pharmaceuticals. In contrast to the groups described above they only occur in tiny amounts. However, this is predominated by their comparatively high value per mass (Schmidt and Kaltschmitt, 2016).

3.3. *Integrated biorefinery approach*

For the development of a biorefinery concept many factors have to be taken into account. For instance, local climate and soil conditions mainly determine the kinds of plants to be cultivated in theory. This has a significant influence on the respective biorefinery concept as every plant structure or feedstock composition requires specific treatment / conversion / processing technologies. Additionally, markets and infrastructure have to be available to sell especially low-value side-products that have a low transportability.

In order to involve existing plants and structures into this process development small scale agricultural biogas plants offer a huge variety of different optimisation possibilities. But basically there are only three areas to create added-value at conventional biogas plants: Pre-, post-treatment and biogas processing. This is shown in Fig. 2.

3.3.1. *Pre-treatment / feedstock*

In contrast to conventional biogas plants alternative substrates can be used in order to separate valuable fractions within a pre-treatment step. Only the remaining residues are used as a feedstock for biogas fermentation. To allow for an easy and successful implementation such biorefinery concepts should mainly utilize equipment that is simple to maintain and control (e.g. mechanical treatments, physical separation, and aqueous extraction).

3.3.2. *Biogas processing*

As an alternative to direct biogas combustion within a CHP unit additional biogas processing is possible like upgrading to bio-methane to be fed into the natural gas network or e.g. Fischer-Tropsch synthesis to synthetic biofuels (Schmidt and Kaltschmitt, 2016) and thereby create added value. A further option in the far future might be "solar biofuels" by photocatalytic conversion of carbon dioxide to methane in order to increase the methane yield of the biogas fermentation (Roy et al., 2010), or even further photocatalytic oxidation to hydrogen (Cargnello et al., 2011). However, these processes are still in early development stage (TRL 1–3) and are therefore not applicable for application on agricultural biogas plants yet.

3.3.3. *Post-treatment*

The remaining material stream (digestate) after passing the fermentation unit can still be used as soil conditioner and organic / mineral fertilizer. Compared to the direct use as realized today a processing can be realized to provide standardized and easily marketable products. This includes for example a solid-liquid separation

Thus the energetic utilization of biomass by biogas production becomes economically less important and is only considered as a sink for the residual biomass.

4. Example: clover biorefinery

Here, catch crops are chosen as an exemplary biomass source for the assessment of a respective biorefinery concept. Catch crops are characterized by the fact that they do not cause additional land consumption because they are cultivated in-between the main crops. Such catch crops belong to the plant families of legumes (e.g. clover), grasses (e.g. rye grass), crucifers (e.g. mustard) or composite plants (e.g. safflower). The composition of the substrates assumed to be grown as a catch crop for this study, clover and safflower, is given in the Appendix A (Table A1). Catch crop cultivation is often undertaken with the aim of preserving nutrients, reducing soil erosion, suppressing other plants and improving the humus balance. It has been shown that catch crops are

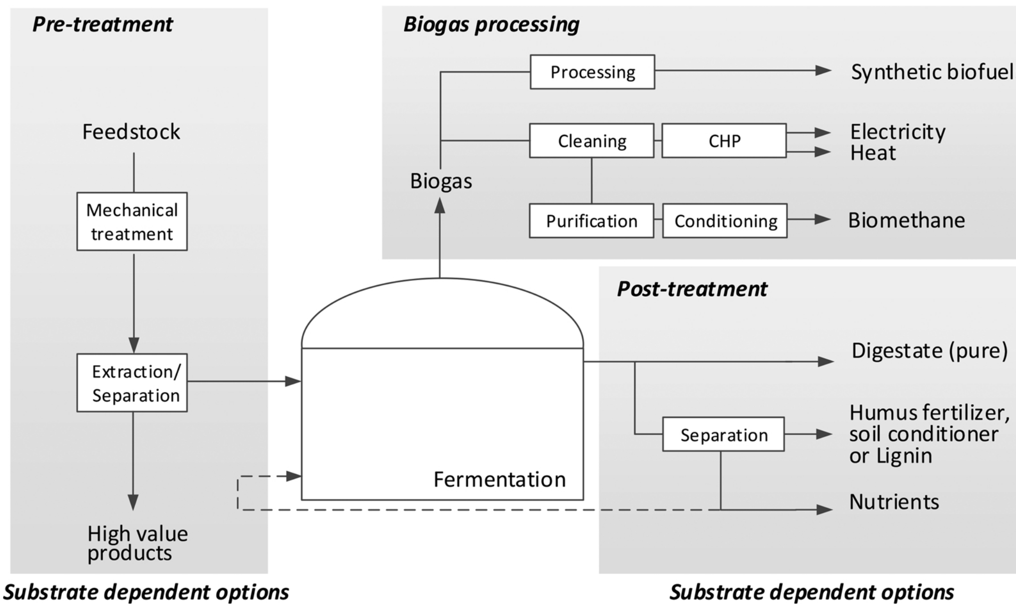

Fig. 2. Overview of processing options in integrated biorefineries based on agricultural biogas plants, differentiated in pre- / post-treatment and biogas processing modified from (Kaltschmitt, 2018).

typically suitable for the use as a substrate for biogas plants.

Clover grass is suitable for cultivation as a catch crop, especially due to its ability to bind atmospheric nitrogen that enriches plant-available nitrogen in the soil. Clover grass thus contributes to the nitrogen availability for the subsequent culture (Menke and Rauber, 2015). Clover is usually sowed after harvesting the main crop (e.g. maize, cereals) in July or August. The later sowed, the longer cultivation takes. Clover is then harvested in several cuts until the onset of winter and so far mainly used as feed due to its relatively high protein content (12–20 %-DM (dry matter), depending on the composition of the clover mixture, the cut number and fertilization). Clover can also be used for biogas production. The market price for untreated clover grass (1st cut) averaged 100 €/ha in 2017 (Federal Ministry for Agriculture, Food and Consumer Protection in Baden-Württemberg 2016) resulting in a revenue of 26 €/t_{DM} by assuming a yield of 20–27 t_{FM}/ha (Dilger and Faulhaber, 2006).

4.1. Reference case

For the evaluation of the clover biorefinery concept generating added-value and increasing the amount of material utilization, a reference case is defined. Thus, for this reference case it is assumed that only biogas is produced from clover grass. The provided biogas is then converted into electricity and heat in a combined heat and power (CHP) plant. The resulting digestate is applied without treatment to the surrounding fields. The theoretical biogas potential of clover grass (1st cut) is 647 L/kg_{oDM} (organic dry matter), see Table A1, and hence comparable to maize silage. The assessment parameters are calculated as follows (Table 1).

- Biogas production form grass (including clover grass) is already implemented in an industrial scale. The development level of biogas conversion to heat and electricity in coupled processes is state of technology and numerously operated globally. Thus the technology readiness level *TRL* can be defined with 9.
- The biogas as the first output stream is converted into electrical energy in a combined heat and power plant (CHP) with an average electrical efficiency of 38% (Aschmann and Effenberger, 2012). The revenue for electricity from biogas can be assumed with 0.0644 €/kWh (The German Federal Network Agency for Electricity, Gas, Telecommunications, Post and Railway 2014), thus the revenue for the biogas used in CHP can be estimated with 0.024 €/kWh. The price for the digestate as the second output stream depends on the local market demands. In the worst case, the biogas plant operator has to pay for digestate distribution (Rolink, 2013, 2013). In most cases, however, a cost-neutral release of digestate to the surrounding farms takes place due to the fertilizer value of this material. Thus, no increase of the substrate value (*VSV*) is assumed for the direct application of the digestate. The variation of the substrate value (*VSV*) for the total reference process is 3.4 (this means the clover grass value increases by factor 3.4 due to biogas production).
- For the estimation of the material biomass utilization efficiency BUE_M, the lignin contained in the digestate as well as the nutrients (N, P, K) contributing to the improvement of the soil quality in a direct application are taken into account. For the reference case the BUE_M is 16.3%-DM of the clover biomass.
- The energetic biomass utilization efficiency BUE_E of thiy process is measured by the produced methane mass and is 21.7%-DM based on the initial clover biomass.
- The electricity demand of the biogas fermentation is 7.9% of the produced electrical energy in the CHP (assuming 38 % electrical efficiency of the CHP) (Gemmeke 2010). The heat energy demand is 11.5% of produced heat in the CHP (assuming 50% thermal efficiency). This is subtracted from the generated biogas amount. Thus the demand for auxiliaries per ton dry clover mass is 91 kW h/t electricity and 626 kW h/t heat.

4.2. Clover biorefinery

An alternative biomass utilization of clover grass in terms of protein isolation, biogas production, fertilizer production and digestate recycling is discussed exemplarily below.

4.2.1. Pre-treatment

Proteins can be separated from clover (fresh or silage) and sold as high-quality feed. The first processing step is a mechanical pre-

Table 1
Assessment parameter results for the clover biorefinery case study ("C" column) and its corresponding reference case ("R" column). Only one utilization efficiency ($BUE_{M\ or\ E}$) is possible per step. Electricity and heat demand are only shown for the case study as difference to the reference case.

Clover biorefinery	*TRL*		*VSV*		*BUE$_M$* (%)		*BUE$_E$* (%)		Electricity (kWh)	Heat (MJ)
	R	C	R	C	R	C	R	C	C	C
Protein separation	–	7		1.5	–	4.3			23	285
Biogas production	9	9	3.4	3.2			21.7	20.4	86	590
(Partial) digestate conditioning	–	9		0.8	16.3	15.6			46 – 64	–
Total	9	7	3.4	5.5	16.3	19.9	21.7	20.4	155 – 173	875

treatment where the clover grass is pressed and press juice is obtained. This press juice has a protein content of approx. 264 g/kg_{DM} with 5.9% dry matter content (Andersen and Kiel, 2000; Kamm, 2009). The proteins can then be precipitated by coagulation (denaturation and formation of agglomerates) with hot steam within a countercurrent process and separated by a solid-liquid separation within a decanter (Kamm, 2009). This concept can be assessed as follows (Table 1).

- The development level of such a protein separation is estimated with a technology readiness level *TRL* of 7. This is justified by the fact that such a plant for protein separation based on the process mentioned above with a capacity of 5000 t_{FM}/a is successfully operated since 2007 (Biowert Industrie GmbH, 2017).
- The protein concentrate contains about twice as much protein as soybean meal (i.e. the "classical" protein cattle feed). The market price can therefore be assumed with double the soybean meal price (soy market price 02/2017: 357 €/t_{soy}). The substrate value (*VSV*) is increased by a factor of 1.5 due to the protein product.
- From one ton of clover grass (DM) about 70 kg of protein concentrate can be produced with a protein content of about 60%-DM. This results in a material biomass utilization efficiency BUE_M of 4.3%-DM based on the initial clover biomass (Kamm, 2009).
- The energy required is approximately 23 kW h/t of electricity and 285 MJ/t of heat (steam) per ton of clover grass (DM) (Kamm et al., 2009). No chemical additives are needed; the required apparatuses are a press, a coagulator, a decanter and a drying device. Thus the demand for auxiliaries is limited to electricity and heat.

4.2.2. Biogas processing

The residue from the protein separation is fermented within the existing biogas plant. The biogas is converted into electrical energy in a combined heat and power (CHP) plant according to the reference case. Assuming that 74% of the clover grass proteins remain in the residue due to the simple and thus cheap separation method, the theoretical potential for biogas formation can be estimated at 609 m^3/t_{DM} with a methane content of approximately 52%.

- The *TRL* can be defined with 9 according to the reference case.
- The substrate value (*VSV*) of clover grass increases by factor 3.2 due to the biogas production step.
- The energetic biomass utilization efficiency BUE_E of biogas production is measured by the produced methane and is 20.4%-DM based on the initial clover biomass.
- The demand for auxiliaries for the biogas production can be calculated according to the reference case. Per ton dry clover mass 86 kW h/t electricity and 590 kW h/t heat are needed.

4.2.3. Post-treatment

After anaerobic fermentation the digestate mainly consists of inorganic substances (minerals and nutrients) as well as lignin which cannot be digested; additionally some undigested other biopolymers might be contained due to an incomplete anaerobic digestion due to economic constraints. These remaining organic components are the reason why the digestate can be further processed to form a humus fertilizer (i.e. compost). Therefore, the solid phase is separated from the liquid phase in a decanter or centrifuge. To make the solid material stable typically a composting process is realized. Due to the remaining content of organic components, the composted solid phase of the digestate contains a relatively high proportion of bound carbon, which favors the reproduction of humus in agricultural soil. It can therefore be used as an organic soil conditioner. The nutrients contained within this material are also responsible for an additional fertilizing effect (Sensel and Wragge, 2008). In addition, the fertilizer can be transported to much longer distances due to the reduced water content compared to the untreated digestate. The separated liquid phase can either be recycled as process water into the biogas plant and / or discharged as a liquid NPK fertilizer on the surrounding agricultural fields. This approach can be evaluated as follows (Table 1).

- Digestate treatment is already state of the art in many biogas plants; i.e. the technology readiness level *TRL* can be assumed to be 9.
- The total revenue for the humus fertilizer consists of the nutrient revenue and the revenue for the humus effect and sums up to ca. 17.4 €/t clover (DM) (Kehres 2013) (assuming 63% C in lignin). Accordingly, the substrate value (*VSV*) increases by a factor of 0.8 due to the humus fertilizer. For the calculation of the *VSV* it is assumed that two-thirds of the mineral components in the digestate are dissolved (N and K are completely dissolved, P is dissolved by approximately two-third and Mg is completely bound). By decanting the digestate, about 10%-FM are separated as humus fertilizer with 25% dry matter content.
- The material biomass utilization efficiency BUE_M of the humus fertilizer (only lignin and mineral components are taken into account as usable material) is 10.6%-DM based on the initial clover biomass (DM). The humus fertilizer contains 0.5 % P, 0.9 % Mg, 1.0 % K and 0.7 % N (dry matter base); thus, the product can be declared as organic mineral fertilizer according to the German DüMV 2012 (The German Federal Ministry of Food, Agriculture and Consumer Protection, 2012). The liquid phase can be applied free of charge to adjacent fields, which increases the material biomass utilization efficiency BUE_M of the digestate treatment to 15.6% of the initial clover grass (DM).
- The decanter energy demand depends on the desired dry matter content of the solid phase and is, for example, between 5 and 7 kW h/t digestate with 25–30 % dry matter content (GEA Westfalia Separator Group GmbH, 2018). If a biogas production with 10% DM is assumed, the digestate still contains 4% DM; thus the energy demand for solid phase separation is 46–64 kW h/t clover grass (DM). Thus the demand for auxiliaries sums up to 51–71 kW h/t.

4.3. Comparison

The concept of clover utilization offers an enhanced revenue compared to the reference concept. The material biomass utilization

efficiency BUE_M as well as the variation in substrate value (*VSV*) are increased compared to the reference case (Table 1).

- The *TRL* of the advanced plant concept decreased slightly from 9 to 7 due to the transition from the reference concept to the clover biorefinery concept. But a last scale-up is realistic in a reasonable timeframe and the risk is limited since a pilot plant is already in operation. Also, the complexity of the components needed for the protein separation is rated as medium to low (mostly mechanical processing steps). However, the investment and operating costs are to be considered separately despite low energy and auxiliary supplies.
- Despite the relatively low protein yield of 42 kg/t clover (DM) this process step shows an increase in substrate value *VSV* of 1.5, without significantly decreasing the *VSV* of the biogas production from 3.4 to 3.2. Taking into account the subsequent biogas production and additional processing of the fermentation residue into soil conditioner, the *VSV* of the total plant is increased from 3.4 (reference) to 5.5 (biorefinery concept) and thus by 62%.
- The material utilization of the protein fraction allows to create added-value; i.e. the separation and material utilization of the protein fraction increase the overall BUE_M of the entire plant around 16–20 %-DM. At the same time, the BUE_E is reduced by 6–20 %-DM.

In summary, the assessed indicators show that this concept offers a considerable potential for added-value regarding the utilized substrate clover and demonstrate its application in an integrated biogas biorefinery through the application of relatively simple additional processing steps.

5. Example: safflower biorefinery

For this second example safflower, a composite plant with yellow flowers, is investigated. Safflower can be cultivated also as a catch crop from April to August (e.g. after winter wheat). The flowers of this cash crop contain between 0.3 and 0.9%-DM Carthamidine (safflower yellow) and up to 36%-DM Carthamin (safflower red) (Schweppe, 1993; Cardon, 2007; Nagaraj, 2009; Machewad et al., 2012; Jadhav and Joshi, 2015). While Carthamin is not light-resistant and also hard to extract, Carthamidine can be separated from the flower by a simple aqueous extraction and used as a food colorant (trade name: *C.I. Natural Yellow 5*). For safflower flowers in Asian markets, a revenue of about 4.1 €/kg flowers (fresh mass) can be achieved (Rajvanshi 2004). The safflower straw price is assumed to be equivalent to the wheat straw price (82 €/t, (Krauß, 2016). This results in a total revenue of 95 €/t for whole safflower plant by assuming 3.3 kg/t dry flower mass per ton whole safflower plant (always DM-basis) (Nagaraj et al., 2001; Dietze et al., 2008; Nagaraj, 2009).

5.1. Reference case

Also the safflower biorefinery concept is compared to the reference case. For this base case it is assumed that biogas is produced directly from safflower and the digestate is applied without further treatment to the surrounding fields. The provided biogas is converted to heat and electricity within a CHP plant. The theoretical biogas potential of safflower (whole plant) is 547 L/kg$_{oDM}$ (Table A1). The assessment parameters are calculated according to the clover reference case (Table 2).

- Biogas production form straw is already implemented on an industrial scale (Verbio, 2014). Thus the *TRL* is 8–9.
- The substrate value (*VSV*) of safflower biomass increases by the factor 0.7 due to biogas production.
- The material biomass utilization efficiency BUE_M for the reference case is 16.3%-DM of the whole safflower biomass due to digestate recycling to the fields.
- The energetic biomass utilization efficiency BUE_E of the reference process is measured by the produced methane mass and is 19.5%-DM based on the initial safflower biomass.
- The demand for auxiliaries per ton dry safflower mass is 81 kW h/t electricity and 561 kW h/t heat.

5.2. Safflower biorefinery

An alternative safflower biorefinery concept is demonstrated based on safflower yellow (Carthamidine) dye production. Additionally, the biogas is further processed to biomethane. The digestate is recycled to the surrounding fields.

5.2.1. Pre-treatment

For the safflower dye extraction, safflower flowers are mechanically pretreated by drying and crushing after harvesting (Heindl and Hoppe, 2010). The aqueous extraction of Carthamidine takes place at about 40 °C (Machewad et al., 2013). Afterwards the produced extract is evaporated. This approach can be evaluated as follows (Table 2).

- The dye separation is rated with a technology readiness level *TRL* of 7. This is justified because Carthamidine from safflower flowers is already available on the market as a food colorant and used for dyeing textiles (Machewad et al., 2013). But the process to be operated on a small scale as well as the harvesting technology still needs to be optimized and further developed to reduce the overall costs.
- By assuming an extraction yield of 80% and a Carthamidine price of 72–218 €/kg (Shaanxi Fuheng (FH) Biotechnology Co., Ltd. 2017), the substrate value (*VSV*) is increased by a factor between 0.7 and 2.1 due to the commercialization of the Carthamidine extract.

Table 2
Assessment parameter results for the safflower biorefinery case study ("C" column) and its corresponding reference case ("R" column). Only one utilization efficiency ($BUE_{M\ or\ E}$) is possible per step. Electricity and heat demand are only shown for the case study as difference to the reference case. Additionally, 0.8 kg per ton of dry substrate is needed for the biogas purification to produce bio-methane.

Safflower	*TRL*		*VSV*		BUE_M (%)		BUE_E (%)		Electricity (kWh)	Heat (MJ)
biorefinery	R	C	R	C	R	C	R	C	C	C
Colorant separation		7		0.7 – 2.1	–	0,1			10	138 – 175
Biogas production (and biomethane purification)	8	8	0.7	1.8			19.5	19.5	177 – 199	561
Direct digestate fertilizer	8	8	–	–	25,8	25.8				
Total	8	7	0.7	2.5 – 3.9	25.8	25.9		19.5	187 – 209	700 – 736

- The material biomass utilization efficiency BUE_M is < 0.1%-DM based on the whole safflower plant dry mass.
- The energy demand per ton dry safflower mass for drying, extraction and evaporation can be estimated with 139–175 MJ/t heat demand and at 10 kW h/t electrical energy demand (Heindl and Müller, 2010).

5.2.2. Biomethane processing

Safflower straw and residuals from Carthamidine extraction are fermented in the existing biogas plant. The biogas potential is approx. 547 m^3/t_{DM} with 52% methane content. To feed biomethane into the natural gas grid, first sulphur is removed to a certain degree by biological desulfurisation. Then CO_2 separation is realized by pressure swing adsorption (PSA). Additionally, an adsorptive process with regeneration of the adsorbent (e.g. silica gel) is assumed for the biomethane drying (German Biomass Research Centre 2014). Fine desulfurisation is done subsequently by means of activated carbon to maintain the sulphur limits defined by the grid operator resp. the government. After adjusting the pressure and the calorific value (Wobbe index), the biomethane can be fed into the existing natural gas grid.

- The state of technology of a biomethane production from biogas can be assessed with a technology readiness level *TRL* of 9; the process is already implemented on an industrial scale (Krahl et al., 2014). However, in this case it is still based on a straw fermentation that has a TRL of 8 (see reference Section 5.1)
- The selling price of biomethane in the German natural gas network is around 0.0644 €/kWh (The German Federal Network Agency for Electricity, Gas, Telecommunications, Post and Railway 2014). Based on this the substrate value (*VSV*) is increased by a factor of 1.8 due to the biomethane production assumed here.
- The biomethane production corresponds to an energetic biomass utilization efficiency BUE_E of 19.5%-DM based on the initial whole safflower dry mass. This value is the same as within the reference case since only the methane from the biogas has been utilized.
- The electrical energy requirement of the treatment is 0.17 to 0.23 kW h/m^3 biogas (87–119 kW h/t dry safflower mass) (German research centre for biomass 2015)(German Biomass Research Centre 2014). Fine desulfurisation requires around 500 kg/a of activated carbon (500 kW plant) (equals 0.3 kg/t dry safflower mass) (Koop, 2016). Thus the necessary demand for auxiliaries consists of electricity and activated carbon.

5.2.3. Post-treatment

The digestate is distributed to the surrounding agricultural fields without further processing.

- Digestates are already used as a fertilizer of agricultural areas (*TRL* 9).
- No increase of the substrate value (*VSV*) is assumed for the direct application of the digestate.
- The material biomass utilization efficiency (BUE_M) of digestate recycling is 25.8%-DM based on the initial whole safflower dry mass.
- No demand for auxiliaries are given – except of the diesel fuel needed for transportation (this is neglected here because no assumptions have been made for the necessary transport distances).

5.3. Comparison

The concept for dye recovery is also positive compared to its corresponding reference case. The main advantage is that the added-value is mainly generated by a secondary plant constituent that only makes up a tiny mass fraction of the plant. Thus, the biogas fermentation is not significantly influenced by its separation.

- The technology readiness level *TRL* of the overall process is slightly lower than the reference (7 instead of 8). While biomethane treatments and digestate application are state-of-the-art in industry, there is still room for improvement in the harvesting techniques of safflower flowers as well as the processing on a small scale in agriculture to provide a marketable product.
- The low amount of separated safflower flowers is outweighed by a considerable revenue per gram. Hence, the yellow Carthamidine dye paste produced from the extracts of safflower flowers increase the substrate value (*VSV*) by a factor of up to 2.1. In addition, the processing of biogas into biomethane further increase the substrate value. Thus the overall process achieves a *VSV* of 3.9.
- The utilization efficiencies BUE_M & BUE_E don't change in comparison with the reference case, since the dye-containing flowers only account for a tiny fraction of the overall plant mass.

In consequence, biomethane purification and colorant extraction from safflower offer a large potential to increase the value of the used feedstock without having a large impact on the biogas fermentation. It would easily be possible to generate further value by digestate processing (see clover biorefinery (Section 4.1)) depending on the local fertilizer market. In order to broaden the product portfolio to sugar platform chemicals and lignin it would be conceivable to further degrade the lignocellulosic feedstock in terms of more severe pre-treatments (e.g. liquid hot water or the LX-process (Streffer, 2014; Reynolds and Smirnova, 2018)).

6. Conclusion

The biomass demand for food, feed, materials and energy will significantly increase in the future due to growing world population. As a sustainable expansion of cultivation areas is only possible to a very limited extent, it is necessary to optimize the entire biomass utilization. Biorefinery concepts in which a wide variety of biomasses are completely converted to different marketable products with minimal energy input without generating waste, offer appropriate solutions. In developing such concepts, however, the already existing structures and existing biomass conversion facilities should be taken into account and included. Existing biogas plants could represent a core element of such biorefinery concepts to be implemented in the future decentralized in the country side (i.e. small scale approach to minimize the transport distances for the biomass and thus to maximize the biomass potential exploitation). As part of these concepts, the biomass could initially be used for the production of valuable materials and the remaining residues then fed into the biogas process and converted into biogas. The biogas technology thus serves as a sink, in which the resulting organic waste is used.

In order to assess the applicability of such concepts for a specific usage case it is imperative to find significant parameters that indicate values or drawbacks of individual process alternatives. Therefore, an indicator set has been provided applicable for the evaluation each processing step within such innovative biorefinery concepts. In particular, it was shown that catch crops like clover or safflower are valuable resources to be utilized in integrated biogas plants as they can generate added-value without increasing the land use of the biorefinery.

Appendix A

Table A1
Composition of exemplary biogas substrates.

		Clover[a]	Safflower[b]
Dry matter (DM)	%-FM	16	87
Organic DM (oDM)	%-DM	90	96
Components			
Cellulose	%-DM	41	32
Hemicellulose	%-DM	16	19
Lignin	%-DM	10	22
Starch & sugar	%-DM	8	9
Protein	%-DM	16	11
Lipids	%-DM	3	3
Ash	%-DM	10	4
Nutrients			
P	%-DM	0,4	0,2
K	%-DM	3,2	1,4
Mg	%-DM	0,3	0,3
Price	€/t-DM	22	
Biogas potential	m^3/t_{oDM}	647	547
Methane potential	m^3/t_{oDM}	336	283

Sources: [a] (Amon et al., 2004; LfL Bavaria 2013; LKV Bavaria e.V. 2015; Schuster et al., 2015), [b] (Gopalan, 1989; Nagaraj, 2001; Hashemi et al., 2016).

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